



Hydrothermally stable HZSM-5 zeolite catalysts for the transformation of crude bio-oil into hydrocarbons

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ABSTRACT

The hydrothermal stability of two alternative catalysts for the production of hydrocarbons from crude bio-oil has been studied. The valorisation of crude bio-oil from lignocellulosic biomass pyrolysis has been studied by means of a two-step process (thermal-catalytic) and co-feeding methanol, which are strategies that attenuate both the deposition of pyrolytic lignin and catalyst deactivation by coke deposition. A catalyst prepared based on a HZSM-5 zeolite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 80 produces a C_2 – C_4 olefins yield of 32 wt% at 500 °C and with a space time of 0.371 (g of catalyst) h (g of oxygenates)^{−1}. The modification of a HZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30) by impregnation with 1 wt% of Ni produces a yield of aromatics of 42 wt% for the same temperature and space time. These catalysts are very active for bio-oil valorisation (conversion above 90%) with high hydrothermal stability, given that their kinetic behaviour is similar throughout 10 successive reaction–regeneration cycles carried out under severe operating conditions.

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1. Introduction

Biomass and its derivatives generate high expectations for the production of fuels, raw materials for synthesis in the petrochemical industry and fine chemicals [1–3]. In addition to first generation bio-fuels (bio-ethanol and bio-diesel), bio-oil is of interest due to its perspectives for production by lignocellulosic biomass flash pyrolysis and due to the renewable nature of lignocellulosic biomass [4]. The yields in the 450–550 °C range are usually: 60–75 wt% of bio-oil, 15–25 wt% of char and 10–20 wt% of gases [5].

Bio-oil is made up of products from the depolymerisation and fragmentation of lignocellulosic biomass components (cellulose, hemicellulose and lignin), with water content of around 25 wt%, and oxygen content of 45–50 wt%. Over 300 components have been identified by GC–MS [4,6,7], which may be grouped into five families: (1) hydroxyacetaldehydes; (2) hydroxyketones; (3) sugars; (4) carboxylic acids and; (5) phenolic compounds [8]. Its instability (with an increase in viscosity during storage) can be avoided by the addition of 10 wt% of methanol [9].

The valorisation of bio-oil by catalytic transformation in refinery units, such as those of catalytic cracking (FCC) and hydrocracking, is an ambitious aim in order to contribute to the development of the biorefinery concept at large-scale [10–12]. The viability of this

objective has increased in view of the good results of cracking under the operating conditions of FCC units of biomass derivatives, such as glycerol and sorbitol [13].

However, progress in developing the catalytic processes for crude bio-oil valorisation faces an important obstacle due to the deposition, both in the reactor and on the catalyst, of carbonaceous material formed by the polymerisation of lignin-derived components of the biomass. Among these, phenol derivatives are the main components and are especially reactive. This difficulty appears in the vaporization of bio-oil and causes a rapid deactivation of the catalyst and even the plugging of the catalytic bed [14–19]. This problem explains why most of the research on the catalytic transformation of bio-oil is limited to the study of pure components of the bio-oil for obtaining hydrocarbons by deoxygenation-cracking over acid catalysts [20,21] or for obtaining hydrogen by steam reforming over bifunctional catalysts [22–24]. The catalytic transformation of the aqueous fraction of bio-oil (which is separated by increasing the water content over 50 wt%) has also been studied for obtaining hydrocarbons [25] or hydrogen [26,27].

An interesting strategy for the valorisation of crude bio-oil is a two-step process (thermal-catalytic) in series [28] (Fig. 1). Previous papers deal with different aspects of this process [29–32]. The controlled deposition of pyrolytic lignin in the first thermal treatment unit prior to the catalytic reactor (where the volatile compounds are transformed), minimizes the operational problems caused by this deposition, with the main advantage of attenuating catalyst deactivation. This step has already been studied in a

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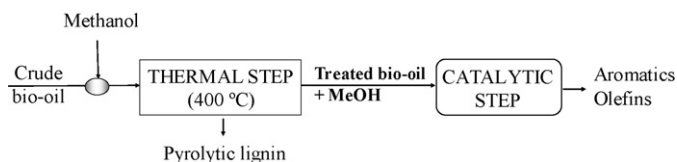


Fig. 1. Two-step process for crude bio-oil valorisation by catalytic transformation for avoiding pyrolytic lignin deposition [29].

previous paper [29], in which the composition and properties of this pyrolytic lignin have been determined and its perspectives for valorisation (essential for the viability of the overall process) have been analysed.

The effect of co-feeding methanol is reported for attenuating pyrolytic lignin deposition. Gayubo et al. [30] have shown in a previous study that the deposition of this pyrolytic lignin is progressively attenuated by increasing the methanol content in the bio-oil/methanol mixture fed into the reactor up to 50 wt%. In addition, methanol co-feeding attenuates coke deposition on the catalyst.

The fluidized bed reactor is suitable for the second step (catalytic transformation) of this process, given that it has the following advantages: (i) the bed is isothermal; (ii) the particle movement avoids plugging by pyrolytic lignin deposition; (iii) the effect of steam as an agent for attenuating coke deposition is more efficient, as in the transformation of methanol and other oxygenate compounds [33], and; (iv) the activity of the particles is uniform in the bed.

This catalytic transformation step has already been studied, in order to discriminate catalysts for the selective production of light olefins [31] or aromatics [32], and catalysts prepared with HZSM-5 zeolites are suitable for both objectives. It has been widely reported that catalysts based on HZSM-5 zeolites are suitable for the transformation into hydrocarbons of methanol [34,35], ethanol [36], other pure oxygenated compounds [37] and bio-oil components [20,21], due to a good balance between the acid strength (moderate) and shape selectivity. This shape selectivity allows the access of most bio-oil components and restricts the evolution of coke precursors, which is a consequence of its three-dimensional crystalline structure, without cages in the intersections between channels [38]. However, the transformation of both crude bio-oil and the bio-oil/methanol mixture requires temperatures above 400 °C and there is a high water content in the reaction medium due to both the water fed with the bio-oil and that generated by oxygenates dehydration. These previous papers prove that the increase of water content in the reaction medium attenuates coke deposition, although it also attenuates the catalytic transformation of bio-oil oxygenates [30–32]. Moreover, HZSM-5 zeolite catalysts undergoes irreversible deactivation by dealumination under high temperature and high water content conditions, which has been determined in the catalytic transformation of pure oxygenates (methanol, ethanol) into hydrocarbons [36,39]. Under these conditions, the thermal stability of the catalyst is a key requirement for the viability of the process. Moreover, given the rapid deactivation by coke deposition, it is essential to uphold the kinetic performance of the catalyst in successive reaction–regeneration cycles without irreversible deactivation by dealumination of the zeolite.

The performance of two catalysts in the two-step process (Fig. 1) has been studied in this paper by operating in reaction–regeneration cycles in the catalytic transformation step. The catalysts have been selected based on their selectivity for the production of light olefins [31] and aromatics [32]. This study determines the limit reaction conditions (temperature and water content in the feed) for the hydrothermal stability of both catalysts.

Table 1

Component families (wt% by mass unit of organic components) in the crude bio-oil.

Components	wt%
Acetic acid	15.3
Acetone	5.3
Other ketones	21.8
Other acids and esters	10.8
Hydroxyacetaldehyde	10.6
Other aldehydes	8.7
Phenols	8.2
Alcohols	11.6
Ethers	0.9
Levoglucosan	3.9
Others	1.3
Unidentified	1.6

2. Experimental

2.1. Bio-oil composition

The bio-oil has been obtained at 450 °C using a N₂ stream in a pilot plant provided with a conical spouted bed reactor [6,40], by feeding pine (*pinus insignis*) sawdust with a particle size between 0.8 and 2 mm. The bio-oil used in this study corresponds to a 75–76 wt% fraction of the whole bio-oil, given that in order to attain product reproducibility the bio-oil studied is that collected in the condenser and in the ice water trap, whereas that retained in the coalescence filter has been discarded. The composition of the crude bio-oil (Table 1) was determined by GC/MS analysis in a GC/MS device (Shimadzu QP2010S) provided with a TBR-1MS column. The detailed composition of the crude bio-oil (wt% of individual components) is given elsewhere [29]. Product identification has been carried out by means of the NIST 147 library and the correction factors for the chromatographic analysis have been determined by using 18 pattern mixtures containing the main components. Water content (48 wt% in the crude bio-oil) has been measured by gas chromatography (Agilent Micro GC 3000).

2.2. Reaction equipment and product analysis

The reaction equipment is shown in Fig. 2. The thermal and catalytic cracking of bio-oil is carried out on-line in two separate units. In the first unit (cylindrical tube made of S-316 stainless steel with an internal diameter of 5/8 in., whose inlet is cooled with water in order to avoid heating of the bio-oil/methanol mixture in the 1/16 in. feeding pipe and prevent the condensation of pyrolytic lignin in this feeding line), bio-oil is heated and a carbonaceous material is deposited on a bed of glass spheres at 400 °C. This material (denoted as pyrolytic lignin) is formed by the polymerisation of lignin-derived components in the bio-oil. The amount of pyrolytic lignin deposited in this unit during the reaction step for a feed of bio-oil (40 wt%) and aqueous methanol (60 wt%) is 12 wt% of the bio-oil in the feed. This result is obtained in all experiments since both the conditions at the thermal treatment step and feeding conditions are the same. The catalytic transformation of the volatile compounds leaving the first unit is carried out in the second unit. These are bio-oil oxygenate components with a small amount of gaseous products formed by thermal cracking, whose concentrations are 3.2 wt% of CO, 2.8 wt% of CO₂ and 0.7 wt% of CH₄. This second unit is a fluidized bed reactor (a vertical cylinder of S-316 stainless steel with an internal diameter of 20 mm and a total length of 465 mm) which is located within a ceramic chamber heated by an electrical resistance. The catalytic bed is placed on a porous plate (at 285 mm from the reactor base). It has been proven that a separate step of thermal treatment prior

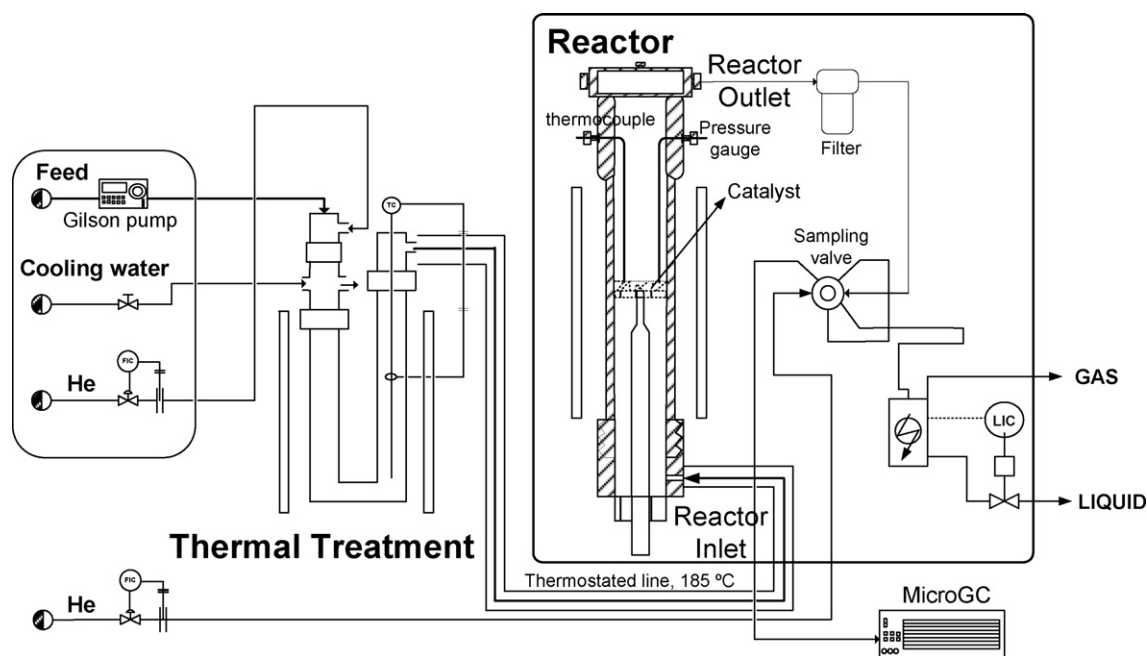


Fig. 2. Reaction equipment.

to the catalytic transformation notably improves the global process of bio-oil upgrading. The advantages of setting this first step for thermal treatment are: (i) it avoids pyrolytic lignin deposition at the catalytic reactor entrance (deposition is not observed in the porous plate or in the access pipes); (ii) it contributes to minimizing coke deposition on the catalyst, leading to an important attenuation of catalyst deactivation; (iii) the bio-oil components degraded in the thermal treatment can subsequently be subjected to another upgrading treatment (by steam activation or pyrolysis) in order to obtain a high quality char, which involves upgrading the entire bio-oil [29].

The on-line analysis of the products that leave the fluidized bed reactor is carried out by gas chromatography: a six-port sampling valve sends every 5 min a representative sample of all products at the reactor outlet through a thermostated line (at 200 °C) to avoid the condensation of heavy compounds. A gas chromatograph (Agilent Micro GC 3000) provided with four modules has been used for the analysis of: (1) permanent gases (O_2 , N_2 , H_2 , CO , CH_4); (2) oxygenates (MeOH, dimethyl ether, CO_2), light olefins (C_2 – C_3) and water; (3) C_2 – C_6 hydrocarbons; (4) C_6 – C_{12} hydrocarbons and all oxygenate compounds in bio-oil. The reaction compounds that do not reach the analysis equipment are cooled in a Peltier condenser (0 °C), from which two streams leave: (1) incondensable compounds that leave the reaction equipment through the gas out-

let and; (2) the liquid fraction that is collected in a vessel placed on a digital balance (Electronic Balances EK-600H). Data gathering and processing are carried out by means of the software Soprane (Version 2.4.b), and taking into account the calibration factors obtained with standard samples of mixtures of the analysed components.

2.3. Catalysts

Three catalysts are used in this study: HZ-30 (which is taken as reference), HZ-80, and NiZ-30. The first two catalysts are prepared from commercial HZSM-5 zeolites (supplied by Zeolyst International) with SiO_2/Al_2O_3 ratios of 30 and 80, respectively. The third one is prepared by modifying the first commercial zeolite by incorporating 1 wt% of Ni, which is a suitable composition for striking a good balance between activity and hydrothermal stability, as has been proven in the transformation of aqueous methanol (with 50 wt% water) at high temperature [41]. The commercial zeolites are supplied in ammonium form and, in order to obtain the acid form, they are calcined following a temperature ramp (up to 570 °C). Impregnation with Ni was carried out by slowly adding a $Ni(NO_3)_2$ solution to the acid zeolite under vacuum (in a Rotavapor) at 80 °C.

The active phases were dried for 24 h at 110 °C and subsequently agglomerated (by wet extrusion) with bentonite (Exaloid)

Table 2
Catalyst properties.

Physical properties of the catalysts				
Catalyst	S_{BET} ($m^2 g^{-1}$)	$V_{m-t-Plot}$ ($cm^3 g^{-1}$)	V_{p-BJH} $17 < d_p(\text{\AA}) < 3000$ ($cm^3 g^{-1}$)	Pore volume distribution, % $<20/20 < d_p(\text{\AA}) < 500/ >500$
HZ-30	267	0.035	0.65	4.5/41.4/54.1
HZ-80	258	0.057	0.58	6.6/37.1/56.3
NiZ-30	178	0.034	0.57	4.2/37.8/58.0
Brönsted/Lewis ratio of the zeolites				
Zeolite	$B/L^{150^\circ C}$	$B/L^{250^\circ C}$	$B/L^{350^\circ C}$	
HZ-30	1.83	2.64	3.07	
HZ-80	0.95	1.96	2.82	
NiZ-30	0.49	0.56	0.61	

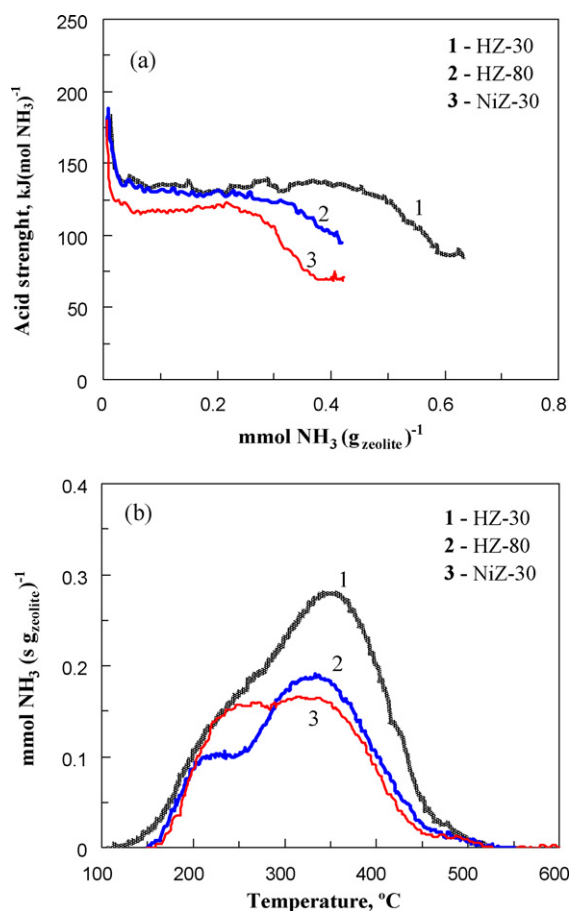


Fig. 3. Catalyst acidity. Graph a, acid strength distribution. Graph b, TPD curves of NH₃ adsorbed at 150 °C.

and using alumina (Prolabo) calcined at 1000 °C as inert charge. The proportion of each component in the catalyst is 25 wt% zeolite, 45 wt% bentonite and 30 wt% alumina. The extrudates were dried at room temperature for 24 h. The particles were subsequently ground and sieved to a size between 0.15 and 0.25 mm, dried at 110 °C for 24 h and calcined at 575 °C for 2 h. This temperature is reached following a heating rate of 5 °C min⁻¹. The agglomeration provides the catalyst with the mechanical strength required to minimize the attrition. In fact, the catalyst mass is practically equal to the initial one after 10 cycles of reaction–regeneration. Moreover, macropores are generated among the zeolite crystals, bentonite and alumina. These macropores and the mesopores of the matrix (bentonite and alumina) enhance bio-oil heavy component diffusion and are very receptive for coke deposition as they avoid the blockage of the zeolite micropores.

The physical properties (Table 2) have been determined by N₂ adsorption–desorption (Micromeritics ASAP 2010) and Hg porosimetry (Micromeritics Autopore 9220). Total acidity and acid strength distribution (Fig. 3a) have been determined by measuring the differential adsorption of NH₃ at 150 °C. Subsequently, TPD (temperature programmed desorption) of the adsorbed NH₃ has been carried out following a temperature ramp of 5 °C min⁻¹ up to 550 °C (Fig. 3b) [42,43]. The equipment used is a thermobalance (TA Instruments SDT 2960) on-line with a mass spectrometer (Balzers Instruments Thermostar). The Brønsted/Lewis acid site ratio (Table 2) has been determined by FTIR (Nicolet 6700 provided with a Specac catalytic chamber), from the ratio between the intensity of the adsorption bands of pyridine at 1545 and 1450 cm⁻¹ analysed at 150, 250 and 350 °C.

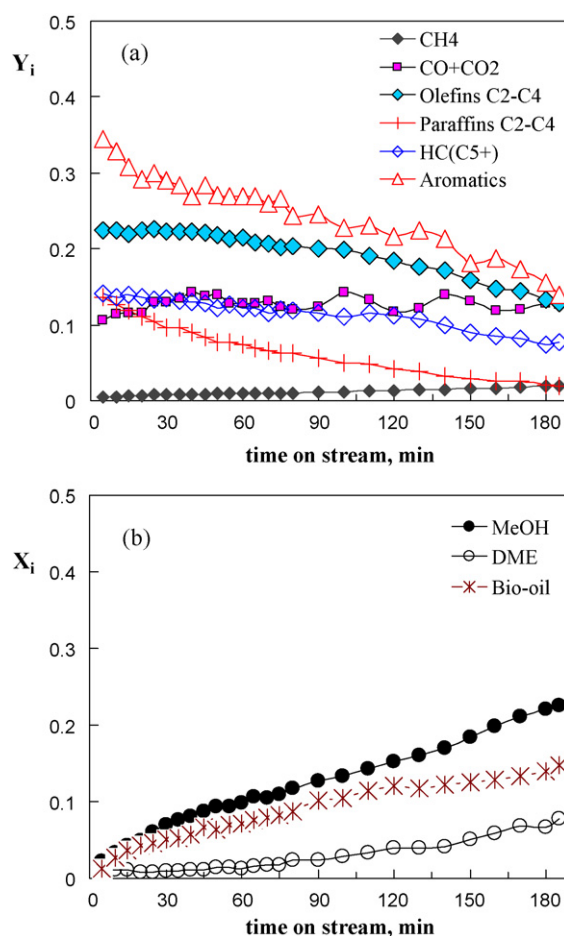


Fig. 4. Evolution with time on stream of product yields (Y_i , graph a) and oxygenate (methanol, DME, bio-oil) concentration at the reactor outlet (X_i , graph b), with HZ-30 catalyst. Reaction conditions: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); 500 °C; $W/F_0 = 0.371$ (g of catalyst) h (g of oxygenates)⁻¹.

The coke deposited on the catalyst has been studied by combustion with air in the TG/MS arrangement described above. Subsequent to a coke aging step in a He stream at 550 °C for 1 h to ensure the reproducibility of the results [44], combustion is carried out with 25% O₂ in He following a temperature ramp of 3 °C min⁻¹ up to 550 °C, and maintaining this temperature for 1 h [43]. Throughout combustion, the following data are monitored: temperature, mass, temperature difference between sample and reference and the intensity in the mass spectrometer for the signals corresponding to the masses 18 (water), 28 (CO), and 44 (CO₂). Signals corresponding to the presence of other compounds, such as SO₂ or NO_x, are negligible.

3. Results

3.1. Hydrocarbon yields

Figs. 4–6 show the results of the evolution with time on stream of product yields, Y_i (“a” graphs) and oxygenate concentration, X_i (“b” graphs). Each figure corresponds to a different catalyst. Bio-oil conversion at zero time on stream is high and similar for the three catalysts under these experimental conditions (500 °C, feed flow rate of 0.15 cm³ min⁻¹, carrier (helium) flow rate of 20 cm³ min⁻¹ and a space time of 0.371 (g of catalyst) h (g of oxygenates)⁻¹). The hydrothermal stability of the catalysts is tested by feeding a mixture of bio-oil (40 wt%) and aqueous methanol (60 wt%) into the process. The aqueous methanol has 50 wt% of water. The thermal treatment

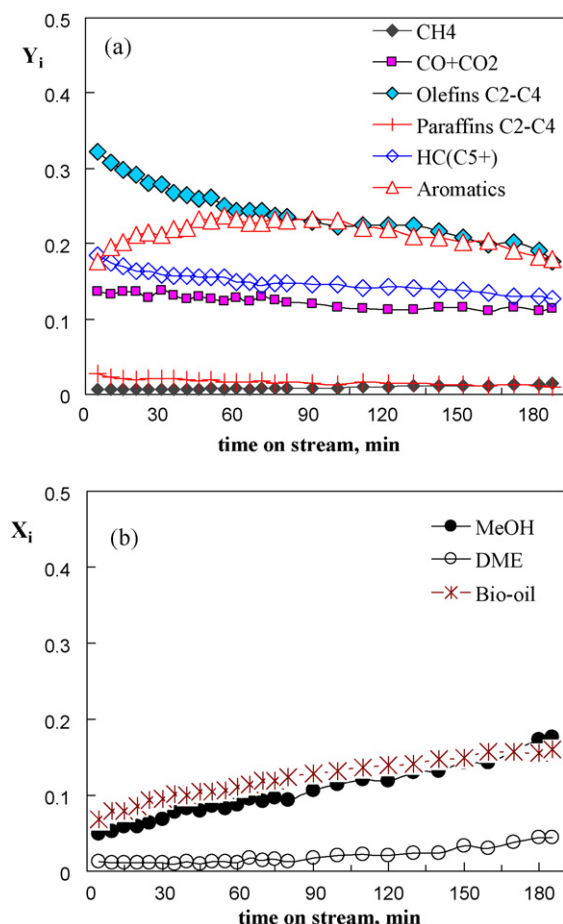


Fig. 5. Evolution with time on stream of product yields (Y_i , graph a) and oxygenate (methanol, DME, bio-oil) concentration at the reactor outlet (X_i , graph b), with HZ-80 catalyst. Reaction conditions: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); 500 °C; $W/F_0 = 0.371$ (g of catalyst) h (g of oxygenates)⁻¹.

step, where the pyrolytic lignin is deposited, has been carried out at 400 °C.

Product concentration (X_i) is defined as the mass fraction of components or lump i at the reactor outlet by mass unit of total component amount, without considering the water in the reaction medium.

Product yields (Y_i) are calculated by mass unit of organic compounds (oxygenates) fed into the fluidized bed catalytic reactor (which is calculated by subtracting the amount of pyrolytic lignin deposited in the thermal treatment unit from the mass flow of oxygenates fed into the two-step system):

$$Y_i = \frac{\text{Mass flow rate of lump } i \text{ at the reactor outlet}}{\text{Mass flow rate of oxygenates fed into the catalytic reactor}} \quad (1)$$

Given that the percentage of organic components in the bio-oil deposited in the first unit (thermal treatment) as “pyrolytic lignin” is 12 wt%, the yields by mass unit of total crude bio-oil in the feed can be easily calculated by multiplying the former yields by a factor of 0.88.

The product lumps studied are: CH₄, CO+CO₂, aromatics, C₂-C₄ olefins, C₂-C₄ paraffins, and non-aromatic C₅+. Dimethyl ether (DME), which is almost in thermodynamic equilibrium with methanol, has been considered as reactant.

A high yield of hydrocarbons at zero time on stream is observed in Fig. 4a for the HZ-30 catalyst: the aromatics yield is 35 wt%, 22 wt% of C₂-C₄ olefins, 13 wt% of C₂-C₄ paraffins and 13 wt% of non-aromatic C₅+, with a negligible yield of CH₄. The formation of CO and CO₂ is noteworthy, with a yield of 11 wt% at zero time on

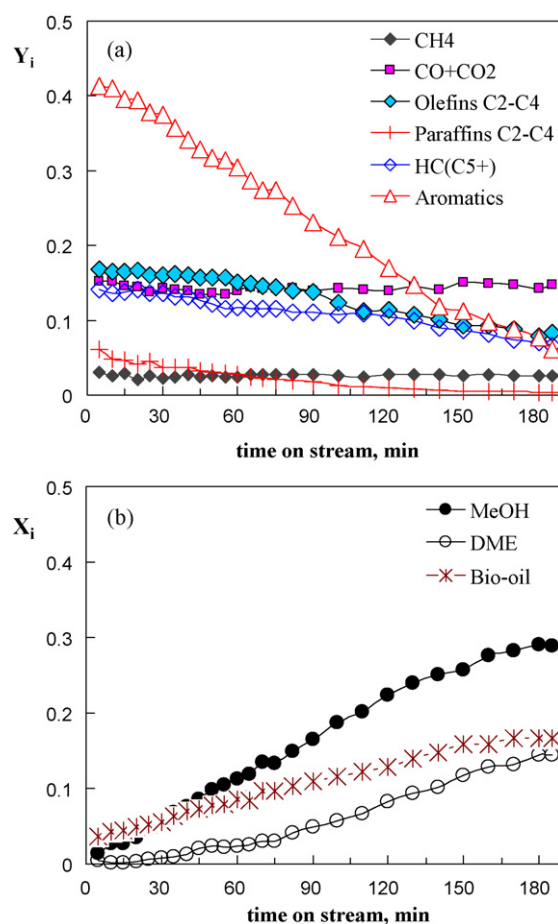


Fig. 6. Evolution with time on stream of product yields (Y_i , graph a) and oxygenate (methanol, DME, bio-oil) concentration at the reactor outlet (X_i , graph b), with NiZ-30 catalyst. Reaction conditions: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); 500 °C; $W/F_0 = 0.371$ (g of catalyst) h (g of oxygenates)⁻¹.

stream. The decarbonylation and decarboxylation reactions have mainly a thermal origin and they are more rapid than the catalytic steps, being enhanced by increasing temperature. It should be noted that this yield of CO and CO₂ attenuates by co-feeding methanol [30] and it is lower (about half) than that obtained at the same temperature by incorporating HZSM-5 zeolite catalysts *in situ* in the pyrolysis reactor [45].

As observed, there is fast deactivation, although it is slower than that obtained without co-feeding methanol [30] or without a thermal step for the separation of pyrolytic lignin [29]. Product lump distribution changes with time on stream (Fig. 4a) due to deactivation, and the concentration of reactants increases (Fig. 4b). The reduction in the yields of aromatics and C₂-C₄ paraffins is significant, whereas the decrease in the yields of non-aromatic C₅ and C₂-C₄ olefins is smaller.

A higher yield of C₂-C₄ olefins at zero time on stream, 32 wt%, is obtained with the HZ-80 catalyst (Fig. 5a) than with HZ-30 catalyst (Fig. 4a) and also its deactivation is noticeably slower. This can be attributed to the lower total acidity (Table 1) and, consequently, to the lower density of acid sites. Moreover, these sites have a slightly lower acid strength (Fig. 3) and lower B/L ratio. These HZ-80 catalyst properties contribute to diminishing acid site blockage by coke and to decreasing its activity in the reactions of coke precursor evolution towards higher molecular weight structures [46,47]. It should be pointed out that propylene concentration (an olefin with increasing commercial interest) is approximately 50 wt% within the C₂-C₄ olefin lump, whereas ethylene and butenes have similar concentrations. Operating conditions and deactivation

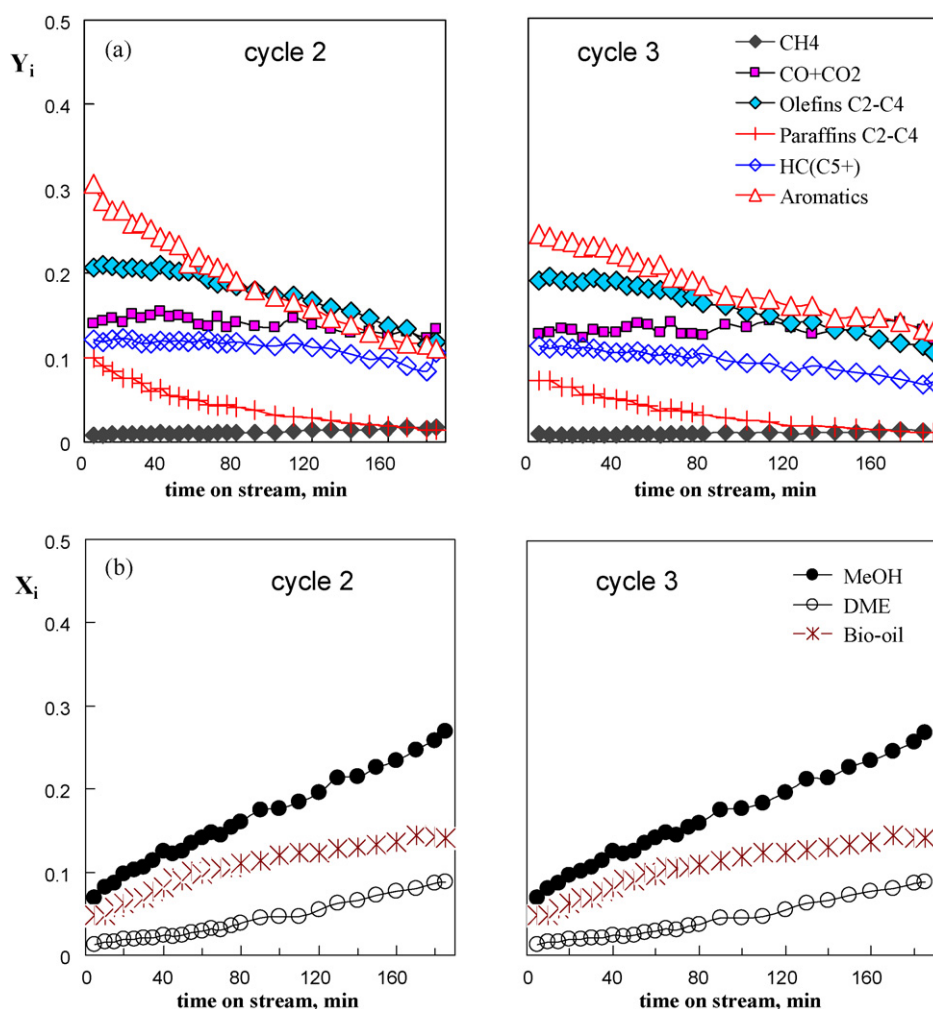


Fig. 7. Evolution with time on stream of product yields (Y_i , graph a) and oxygenate concentration at the reactor outlet (X_i , graph b), in the reaction-regeneration cycles No. 2 and 3. Catalyst, HZ-30. Reaction conditions: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); 500 °C; $W/F_0 = 0.371$ (g of catalyst) h (g of oxygenates) $^{-1}$.

have small impact on olefin distribution. A kinetic scheme valid for the 400–500 °C range was proposed in a previous paper [31], in which CO + CO₂ are primary products apart from C₂–C₄ olefins, aromatics and C₅+ hydrocarbons.

The results in Fig. 6 show that hydrocarbon yields obtained with the NiZ-30 catalyst are lower than those for the catalyst of untreated HZSM-5 zeolite (Fig. 4a). This result is a consequence of the lower total acidity (Table 1) and lower acid strength (Fig. 3) due to Ni incorporation. Nevertheless, due to the dehydrogenating activity of Ni, the aromatic yield at zero time on stream is 42 wt% and the yields of CO + CO₂ and methane are higher than those obtained with the other catalysts. It is noticeable that deactivation is more rapid with this catalyst, which must also be attributed to the dehydrogenating activity of Ni that enhances the condensation of coke precursors. In addition to the high aromatic selectivity of

NiZ-30 catalyst, it is noteworthy that the content of BTX within the aromatic lump is higher than 60 wt% (depending on reaction conditions [32]), which increases the commercial interest of these results. In the reaction mechanism proposed for this catalyst, aromatics are formed from bio-oil via two routes: (i) via direct deoxygenation (dehydration, decarboxylation, decarbonylation)-cracking of high-molecular-weight oxygenates; (ii) by means of the participation of bio-oil oxygenates in the carbon pool mechanism [32]. It should be noted that the yield of hydrogen is very low (below 0.5 wt% at 500 °C, and 0.1 wt% at 450 °C), which is explained by the low temperature for gasification or reforming of bio-oil oxygenates. In addition, Ni content is low (the optimum for the objective of reducing the zeolite acidity), the residence time is low and the rate of competitive reactions catalyzed by acid sites is high.

Table 3

Coke content deposited on the catalysts (C_c , wt%) and yield of coke by mass unit of bio-oil in the feed (Y_c , wt%) at different reaction temperatures. Reaction conditions: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); $W/F_0 = 0.371$ (g of catalyst) h (g of oxygenates) $^{-1}$.

Temperature (°C)	HZ-30		HZ-80		NiZ-30	
	C_c (wt%)	Y_c (wt%)	C_c (wt%)	Y_c (wt%)	C_c (wt%)	Y_c (wt%)
450 (1st reaction step)	3.02	0.39	4.08	0.53	5.28	0.68
500 (3rd reaction step)	2.56	0.33	2.91	0.37	4.38	0.56

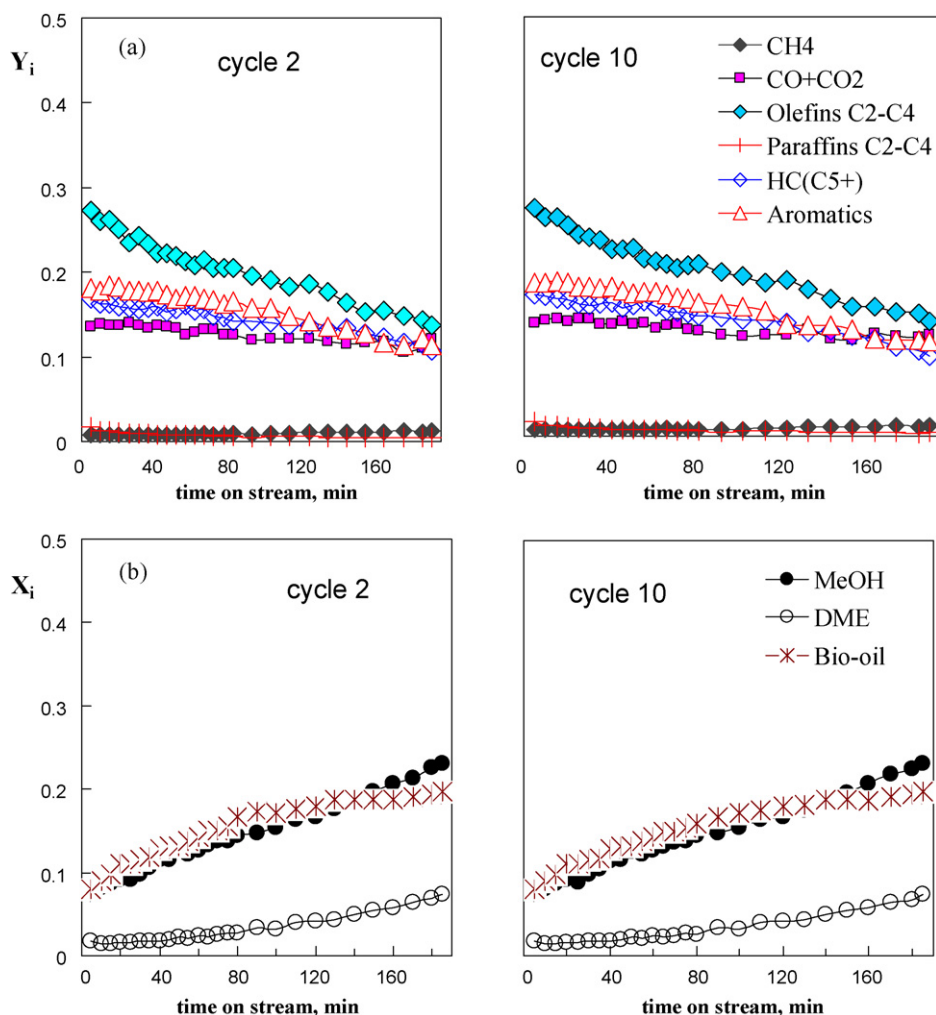


Fig. 8. Evolution with time on stream of product yields (Y_i , graph a) and oxygenate concentration at the reactor outlet (X_i , graph b), in the reaction–regeneration cycles No. 2 and 10. Catalyst, HZ-80. Reaction conditions: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); 500 °C; $W/F_0 = 0.371$ (g of catalyst) h (g of oxygenates)⁻¹.

As mentioned above, bio-oil conversion at zero time on stream under the operating conditions in Figs. 4–6 is high for the three catalysts, with the values of 0.92, 0.82 and 0.81 for HZ-30, HZ-80 and NiZ-30, respectively. This conversion has been calculated from the mass flow rates of bio-oil components at the fluidized bed reactor inlet and outlet:

$$(X_{\text{bio-oil}})_{t=0} = \left[\frac{(m_{\text{bio-oil}})_i - (m_{\text{bio-oil}})_o}{(m_{\text{bio-oil}})_i} \right]_{t=0} \quad (2)$$

where $(m_{\text{bio-oil}})_i$ and $(m_{\text{bio-oil}})_o$ are the mass flow rates of the oxygenates in the bio-oil at the fluidized bed reactor inlet and outlet, respectively, which have been determined from the chromatographic results corresponding to 5 min time on stream.

3.2. Stability of the catalysts in reaction–regeneration cycles

A high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (80 for HZ-80 catalyst) in a HZSM-5 zeolite and its impregnation with Ni are designed to achieve the hydrothermal stability of the catalyst. For the same purpose, a high calcination temperature (575 °C) has also been adopted. These strategies are based on previous studies in which the stability of HZSM-5 zeolites was pursued [41,48].

The results in Figs. 7–9 correspond to experiments in successive reaction–regeneration cycles (up to 10 cycles) carried out with the 3 catalysts under the following operating conditions:

Reaction step: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); 500 °C; space time, 0.371 (g of catalyst) h (g of oxygenates)⁻¹. It should be noted that these reaction conditions (temperature and water content in the reaction medium) are very severe for the catalyst [39].

Regeneration step: combustion with air of the coke deposited on the catalyst at 550 °C for 2 h, to ensure total coke elimination without exceeding the calcination temperature of the catalyst, in order to avoid the irreversible loss of acidity [44].

Graphs a in Figs. 7–9 show the evolution with time on stream of product lump yields, Y_i , and graphs b correspond to the evolution of the concentration of reactants (oxygenates) at the reactor outlet, X_i .

A comparison between the results of the second cycle in Fig. 7 and those in Fig. 4, which correspond to the fresh catalyst, shows that HZ-30 catalyst does not fully recover its activity after the first regeneration, and there is another decrease in activity after the second regeneration. This is typical behaviour in the presence of irreversible deactivation. Under these circumstances, catalyst initial activity steadily decreases in successive reaction–regeneration cycles, although the decrease is less significant as the number of cycles is higher [39,41,48].

The HZ-80 catalyst is hydrothermally stable, although a comparison between the results of the second cycle in Fig. 8 and those

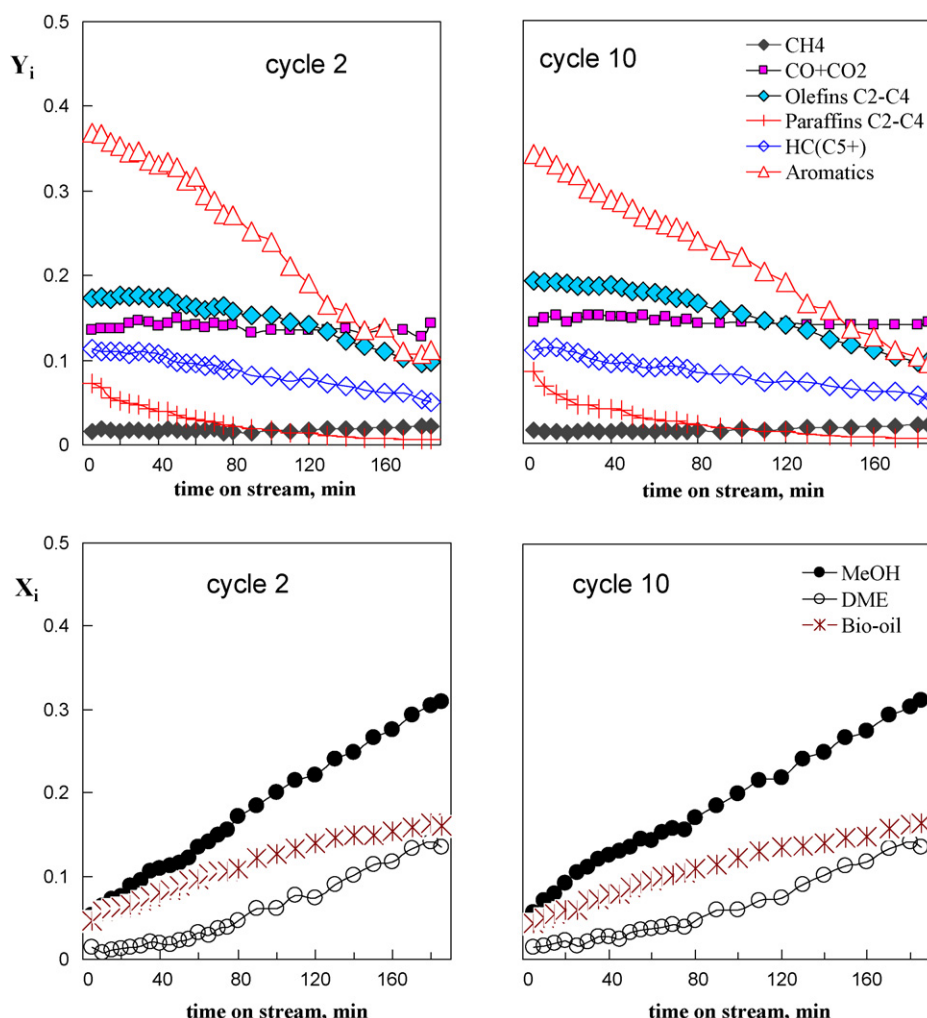


Fig. 9. Evolution with time on stream of product yields (Y_i , graph a) and oxygenate concentration at the reactor outlet (X_i , graph b), in the reaction–regeneration cycles No. 2 and 10. Catalyst, NiZ-30. Reaction conditions: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); 500 °C; $W/F_0 = 0.371$ (g of catalyst) h (g of oxygenates) $^{-1}$.

in Fig. 5 (fresh catalyst) shows that activity does not fully recover after the first regeneration. Nevertheless, the initial activity of the catalyst in the second cycle is maintained in successive cycles, and the results of cycle No. 10 are similar to those of cycle No. 2 (Fig. 8). It should be pointed out that this slight irreversible deactivation in the first reaction–regeneration cycle is typical of HZSM-5 zeolites. This is attributed to the loss of a small fraction of Brønsted strong acid sites, which are presumably removed by dehydroxylation during coke combustion or are unstable Al^{3+} outside the crystalline lattice [39].

The behaviour of NiZ-30 catalyst (Fig. 9) is similar to HZ-80 catalyst, which is evidence of its hydrothermal stability. A small irreversible loss of activity is observed after the first regeneration, but the remaining activity is recovered in successive cycles. It is observed that the kinetic results of reaction step No. 10 (after 9 regenerations) are almost the same as the results of reaction step No. 2.

It should be noted that this catalyst undergoes irreversible deactivation in reaction–regeneration cycles carried out under the aforementioned conditions at 530 °C [49]. Consequently, 500 °C should be considered the ceiling temperature for the reaction step, although higher temperatures are permissible under conditions with lower water content in the reaction medium (by co-feeding bio-oil with pure methanol or with methanol with low water content).

3.3. Coke deposition on the catalysts

The TPO curves corresponding to the combustion of the coke deposited on the three catalysts under different conditions are shown in Fig. 10. Graph a corresponds to the results for the catalysts after the third reaction step at 500 °C, whereas graph b corresponds to the results after the first reaction step at 450 °C.

The high coke content (calculated from the area under the curve in Fig. 10) of NiZ-30 catalyst (Table 3) is consistent with the fast apparent deactivation of this catalyst.

Furthermore, the coke content deposited on HZ-80 catalyst is slightly higher than that on HZ-30 catalyst. This result, which does not agree with the apparent deactivation observed when product yield evolutions with time on stream are compared, is explained by the irreversible deactivation of the HZ-30 catalyst during the reaction step. This irreversible deactivation takes place at 500 °C (Fig. 10a) and at 450 °C (Fig. 10b) and is also responsible for the decrease in coke formation, in which the acid sites play a significant role [46,47].

For HZ-80 and NiZ-30 catalysts, which do not undergo irreversible deactivation, coke content decreases with the increase in temperature. This result is explained by the decrease in the concentration of oxygenates in the reaction medium, which are the main precursors for coke formation [50].

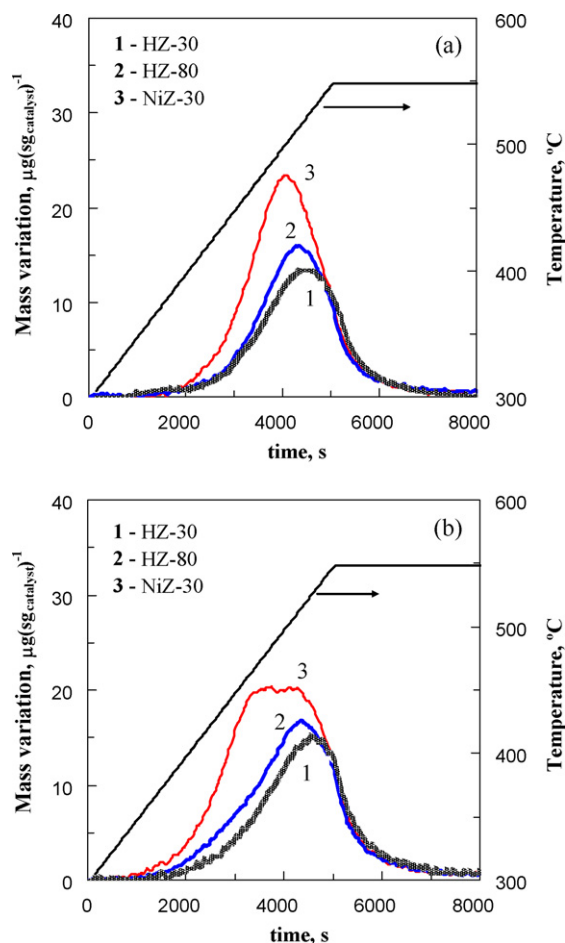


Fig. 10. TPO curves in the combustion of the coke deposited on the different catalysts. Graph a, third reaction step at 500 °C. Graph b, first reaction step at 450 °C. Reaction conditions: feed, bio-oil (40 wt%)/aqueous methanol (60 wt%); $W/F_0 = 0.371$ (g of catalyst) h (g of oxygenates) $^{-1}$.

4. Conclusions

A two-step (thermal-catalytic) process by co-feeding methanol is suitable for attenuating the limitations in crude bio-oil valorisation by catalytic transformation. This means a significant development in the progress of refinery units implementation for the treatment of lignocellulosic biomass derivatives as an alternative to oil. However, a key factor is the availability of hydrothermally stable and selective catalysts for obtaining quality fuels and synthesis raw materials (such as olefins and BTX).

The use of catalysts based on HZSM-5 zeolites with high Si/Al ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) and the modification of HZSM-5 zeolites with low Si/Al ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) by incorporating Ni (1 wt%) are suitable strategies for obtaining hydrothermally stable catalysts. The main reason for this stability is the homogeneous, moderate acid strength and the low density of acid sites in the catalysts, but with the sufficient total acidity required for obtaining hydrocarbons from oxygenates.

HZ-80 and NiZ-30 catalysts are of high hydrothermal stability, which makes them suitable for the catalytic transformation of crude bio-oil stabilized by dilution with methanol. The HZ-80 catalyst produces a high yield of C_2 – C_4 light olefins and the NiZ-30 catalyst produces a high yield of aromatics. These catalysts maintain their kinetic behaviour for up to 10 reaction–regeneration cycles, with the reaction step carried out at 500 °C with high water contents in the reaction medium and regeneration carried out by coke combustion with air at 550 °C.

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References

- [1] G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 106 (2007) 4044.
- [2] A. Corma, S. Iborra, A. Vely, *Chem. Rev.* 107 (2007) 2411.
- [3] P. Maki-Arvela, B. Holmbom, T. Salmi, D.Y. Murzon, *Catal. Rev.* 49 (2007) 197.
- [4] S. Czernik, A.V. Bridgwater, *Energy Fuels* 18 (2004) 590.
- [5] D. Mohan, C.U. Pittman, P.H. Steele, *Energy Fuels* 20 (2006) 848.
- [6] R. Aguado, M. Olazar, M.J. San José, G. Aguirre, J. Bilbao, *Ind. Eng. Chem. Res.* 39 (2000) 1925.
- [7] C. Branca, P. Giudicianni, C. Di Blasi, *Ind. Eng. Chem. Res.* 42 (2003) 3190.
- [8] C. Amen-Chen, H. Pakdel, C. Roy, *Biomass Bioenergy* 79 (2001) 277.
- [9] J.P. Diebold, S. Czernik, *Energy Fuels* 11 (1997) 1081.
- [10] G.W. Huber, A. Corma, *Angew. Chem. Int. Ed.* 46 (2007) 7184.
- [11] M.E. Domine, A.C. van Veen, Y. Schuurman, C. Mirodatos, *Chem. Sus. Chem.* 1 (2008) 179.
- [12] M. Stocker, *Angew. Chem. Int. Ed.* 47 (2008) 9200.
- [13] A. Corma, G.W. Huber, L. Sauvanaud, P. O'Connor, *J. Catal.* 247 (2007) 307.
- [14] R.K. Sharma, N.N. Bakhshi, *Bioresour. Technol.* 45 (1993) 195.
- [15] R.K. Sharma, N.N. Bakhshi, *Energy Fuels* 7 (1993) 306.
- [16] J.D. Adjaye, N.N. Bakhshi, *Fuel Process. Technol.* 45 (1995) 161.
- [17] J.D. Adjaye, N.N. Bakhshi, *Fuel Process. Technol.* 45 (1995) 185.
- [18] J.D. Adjaye, S.P.R. Katikaneni, N.N. Bakhshi, *Fuel Process. Technol.* 48 (1996) 115.
- [19] S. Vitolo, B. Bresci, M. Seggiani, M.G. Gallo, *Fuel* 80 (2001) 17.
- [20] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Aguado, J. Bilbao, *Ind. Eng. Chem. Res.* 43 (2004) 2610.
- [21] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Aguado, M. Olazar, J. Bilbao, *Ind. Eng. Chem. Res.* 43 (2004) 2619.
- [22] C. Rioche, S. Kulkarni, F.C. Meunier, J.P. Breen, R. Burch, *Appl. Catal. B: Environ.* 51 (2005) 130.
- [23] J.R. Galdámez, L. García, R. Bilbao, *Energy Fuels* 19 (2005) 1133.
- [24] F. Bimbela, M. Oliva, J. Ruiz, L. García, J. Arauzo, *J. Anal. Appl. Pyrol.* 79 (2007) 112.
- [25] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Prieto, J. Bilbao, *Energy Fuels* 18 (2004) 1640.
- [26] A.C. Basagiannis, X.E. Verykios, *Catal. Today* 127 (2007) 256.
- [27] P.N. Kechagiopoulos, A.S. Voutetakis, A.A. Lemonidou, I.A. Vasalos, *Ind. Eng. Chem. Res.* 48 (2009) 1400.
- [28] B. Valle, A.G. Gayubo, A. Atutxa, A. Alonso, J. Bilbao, *Int. J. Chem. Reactor Eng.* 5 (2007) A86.
- [29] A.G. Gayubo, B. Valle, A.T. Aguayo, M. Olazar, J. Bilbao, *J. Chem. Technol. Biotechnol.* 85 (2010) 132.
- [30] A.G. Gayubo, B. Valle, A.T. Aguayo, M. Olazar, J. Bilbao, *Energy Fuels* 23 (2009) 4129.
- [31] B. Valle, A.G. Gayubo, A.T. Aguayo, M. Olazar, J. Bilbao, *Ind. Eng. Chem. Res.* 49 (2010) 123.
- [32] B. Valle, A.G. Gayubo, A.T. Aguayo, M. Olazar, J. Bilbao, *Energy Fuels* 24 (2010) 2060.
- [33] A.T. Aguayo, A.G. Gayubo, J.M. Ortega, M. Olazar, J. Bilbao, *Catal. Today* 37 (1997) 239.
- [34] C.D. Chang, *Catal. Rev. Sci. Eng.* 25 (1983) 1.
- [35] M. Stöcker, *Micropor. Mesopor. Mater.* 29 (1999) 3.
- [36] A.T. Aguayo, A.G. Gayubo, A.M. Tarrío, A. Atutxa, J. Bilbao, *J. Chem. Technol. Biotechnol.* 77 (2002) 211.
- [37] C.D. Chang, A.J. Silvestri, *J. Catal.* 47 (1977) 249.
- [38] P.L. Benito, A.G. Gayubo, A.T. Aguayo, M. Olazar, J. Bilbao, *Ind. Eng. Chem. Res.* 35 (1996) 3991.
- [39] A.G. Gayubo, A.T. Aguayo, M. Olazar, R. Vivanco, J. Bilbao, *Chem. Eng. Sci.* 58 (2003) 5239.
- [40] M. Olazar, R. Aguado, M.J. San José, J. Bilbao, *J. Chem. Technol. Biotechnol.* 76 (2001) 469.
- [41] B. Valle, A. Alonso, A. Atutxa, A.G. Gayubo, J. Bilbao, *Catal. Today* 106 (2005) 118.
- [42] A.T. Aguayo, A.G. Gayubo, J. Erena, M. Olazar, J.M. Arandes, J. Bilbao, *J. Chem. Technol. Biotechnol.* 60 (1994) 141.
- [43] A.G. Gayubo, P.L. Benito, A.T. Aguayo, M. Olazar, J. Bilbao, *J. Chem. Technol. Biotechnol.* 65 (1996) 186.
- [44] J.M. Ortega, A.G. Gayubo, A.T. Aguayo, P.L. Benito, J. Bilbao, *Ind. Eng. Chem. Res.* 36 (1997) 60.

- [45] A. Atutxa, R. Aguado, A.G. Gayubo, M. Olazar, J. Bilbao, *Energy Fuels* 19 (2005) 765.
- [46] M. Guisnet, P. Magnoux, *Appl. Catal. A: Gen.* 212 (2001) 83.
- [47] H.S. Cerqueira, G. Caeiro, L. Costa, F. Ramôa Ribeiro, J. Mol. Catal. A: Chem. 292 (2008) 1.
- [48] P.L. Benito, A.T. Aguayo, A.G. Gayubo, J. Bilbao, *Ind. Eng. Chem. Res.* 35 (1996) 2177.
- [49] B. Valle, Obtaining of aromatics and olefins by catalytic transformation of vegetal biomass pyrolysis liquid, Ph.D. Thesis, University of the Basque Country, Bilbao, 2008.
- [50] P.L. Benito, A.G. Gayubo, A.T. Aguayo, M. Castilla, J. Bilbao, *Ind. Eng. Chem. Res.* 35 (1996) 81.